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(19)(CA) **APPLICATION FOR CANADIAN PATENT** (12)

(54) Process for Producing a Sintered Dental Prosthesis

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ABSTRACT OF THE DISCLOSURE

A dental prosthesis having very high density values, that is sintered from noble metal powder mixtures having a bimodal or multimodal particle size distribution is obtained when the drying and sintering processes are carried out in a specific manner. For this purpose the dried dental prosthesis produced from a slip is subjected to a thermal treatment for 5 to 45 minutes at temperatures of between 100 and 400°C, whereupon it is heated to 800°C at an average temperature increase of 50 to 300 k per minute and heated to the sintering temperatures with increases of 20 to 200 K per minute. The sintering temperature lies between ($T_{solidus}$-200) and ($T_{solidus}$-70), $T_{solidus}$ being the solidus temperature of the sintered alloy. The cooling process must be carried out under vacuum or under a protective gas.

The present invention relates to a process for producing a sintered dental prosthesis having a structural matrix of a noble metal powder mixture or of a noble metal alloy powder mixture having a bimodal or multimodal particle size distribution an a predominantly spherical shape. This mixture is stirred with a mixing fluid consisting substantially of water so as to obtain a slip capable of being moulded and compressible by expelling the mixing fluid. The prosthesis is moulded from said slip on a model of the teeth to be supported, applying the technology used in dental ceramics, said model serving as burner support. The slip is subsequently sintered on the model in a graphite box or under a protective gas.

The production of metallic dental prostheses for providing replacement in the case of dental disease and/or after the loss of one or several teeth, as for example, inlays, crowns, that can or cannot be faced with ceramics or plastics, and bridges, is conventionally carried out by means of the so-called "wax melting out process", a first quality casting technique assuring a high degree of accuracy to size.

The advantage of the crowns and bridges thus produced must be seen primarily in the high degree of strength in addition to the accuracy to size and in the existing ductility, which must be assured for large bridge constructions in order to avoid forced ruptures in cases of overstrain.

However, the process per se is very time consuming and the expenditure for material and equipment is high. The necessity of using runners and cast cones requires a markedly increased use of material as compared with the weight of the vast object, and thus repeated reuse of this material can result in changes of the alloying characteristics. In case that this material is not reused it remains as scrap. A further disadvantage of this process is that in the case of flaws in the cast object repairs are not possible and the entire production process, starting with

the wax model, must be repeated.

DE-OS 1915977 describes a process for the sinter production of a metallic dental prosthesis, using a paste consisting of metal powder having a particle size of between 2 and 25 m and a binder acting as adhesive for moulding the dental prosthesis on a model of the teeth to be treated. The dental prosthesis is then sintered. This disadvantage of this process lies in the poor compressibility of the pastes described since the binder acting as an adhesive cannot be expelled by compression methods, such as grooving or shaking. Furthermore, since a powder fraction is used as starting material the density of the green compact is low. Consequently, the sintering process results in a very substantial shrinkage and thus in an unacceptable inaccuracy of fit. The use of very fine powders having a particle size of between 2 and 25 m actually assures a very high degree of sintering activity but it additionally causes high production costs.

The process for the sinter production of a metallic dental prosthesis described in US Patent No. 4, 661, 071 uses powders having a particle size of 5 to 90 m; pasted with a suitable binder, for moulding the metallic dental prosthesis on a model of the teeth to be treated. The production of the model requires a castable self-curing stump mass which must be baked at 1400 to 1600°C prior to the application of the metal powder.

Since conventional dental ceramics ovens reach maximal temperatures of up to approximately 1200°C, a special oven is required. For sintering the metal powder a liquid phase sintering process is used under a vacuum of 1 to 10^{-2}HPa. Since conventional dental ceramics ovens cannot reach this vacuum, a special vacuum oven is required. Furnaces with maximal temperatures of up to 1400°C and furnaces assuring a good vacuum at high temperatures are much more expensive than standard ceramics kilns so that the application of these processes

requires a costly investment for a dental technician. Furthermore, the use of the liquid phase sintering process also causes problems with regard to the natural stability during the sintering process. In order to obtain a compression as fast as possible by rearrangement of the solid component (particles), a liquid phase proportion of at least 30 to 35% is required (R.M. German,, Liquid Phase Sintering, Plenum Press, N.Y. Pages 4, 6 and 80). Analogously to the behaviour in dental baking ceramics chambering and flattening of very delicate details, for example, of an occlusal surface, must be expected and this can cause problems with regard to the contact points, requiring a substantial amount of reworking under certain conditions.

DE-OS- 3532331 describes a process for the sinter production of metallic dental prostheses. By using a powder mixture having a multimodal particle size distribution, which is converted with water into a mouldable and compressible slip, a controlled high density of the green compact is thus attained and the degree of shrinkage during the sintering process remains correspondingly low. This is advantageous for attaining a good accuracy of fit. The use of water as mixing fluid and of a consistency which is very similar to that of slips of dental facing ceramics allows an additional compression by expelling the liquid by means of the technology used in dental ceramics (grooving or the like). The sintering process can be carried out in a conventional dental ceramics oven without great expenditure. This can be achieved by using a graphite box containing the moulded dental prosthesis to be sintered. This graphite box is put into a conventional oven for baking dental ceramics and at the sintering temperature the graphite box assures protection against the oxidation of base metal components of the alloy. However, an adequate reduction of the partial oxygen pressure can also be attained by injecting a protective gas into the ceramics baking oven. On completion of the sintering process the dental prosthesis in the graphite box is cooled in air.

It has been found that that use of powder mixtures of atomized, predominantly spherical noble metal alloys and of precipitated very fine predominantly noble metal powders has disadvantages, namely that with the sintering parameters defined in this process no maximal density values can be attained in the sintered state and that the density of the sintered dental prosthesis decreses distinctly particularly when sintering repeatedly. However, repeated sintering may be necessary when producing bridges in several steps or when making marginal corrections to the edge.

Therefore, it is the present invention provides a process for producing a sintered dental prosthesis having a metallic structural matrix of a noble metal or of a noble metal alloy powder mixture with bimodal or multimodal particle size distribution and a predominantly spherical shape, said mixture being stirred with a mixing fluid consisting substantially of water to a slip capable of being moulded and compressible by expelling the mixing fluid, the prosthesis being moulded with said slip on a model of the teeth to be treated, applying the technology used in dental ceramics, said model serving as burner support, said slip subsequently being sintered on the model in a graphite box or under a protective gas, by means of which optimal density values can be attained in the sintered state, particularly when sintering repeatedly, using conventional equipment and technology.

According to the invention the moulded dental prosthesis is first dried in air for 5 to 25 minutes and then subjected to thermal treatment for 5 to 45 minutes at temperatures of between 100 and 400^{o}C, whereupon it is heated to 800^{o}C at an average temperature increase of 50 to 300 K per minute and above 800^{o}C it is heated to the sintering temperature T at an average temperature increase of 20 to 200 K per minute in air in the graphite box or under a protective gas, said sintering temperature T lying between ($T_{solidus}$-200^{o}C) and ($T_{solidus}$-70^{o}C) $T_{solidus}$ being the solidus temperature of the sintered alloy, the sintering process is

carried out at this temperature for 5 to 45 minutes in the graphite box in air or under a protective gas and thereafter cooling is applied at temperatures of between 800°C and room temperature under protective gas or when using a graphite box even under a vacuum of 50 to 1 HPa.

In one embodiment of the present invention the thermal treatment is carried out at temperatures of between 100 and 400°C for 5 to 25 minutes and the sintering step is carried out for 10 to 30 minutes. Suitably the step of heating to the sintering temperature, the sintering and the cooling are carried out under a protective gas under a partial oxygen pressure lower than 5 x 10^{-2} HPa.

Upon drying the moulded and compressed dental prosthesis in air (15 to 25 minutes) it is put, for example, into a graphite box and subjected to thermal treatment in a temperature range of between 100 and 400°C for 5 to 45 minutes. It is then heated to 800°C at an average temperature increase of 50 to 300 K per minute and from the preheating temperature to the sintering temperature T in air or under protective gas at 20 to 200 K per minute. The sintering temperature T lies between ($T_{solidus}$-200°C) and ($T_{solidus}$-70°C), $T_{solidus}$ being the solidus temperature of the sintered alloy. The sintering process is carried out at this temperature for 5 to 45 minutes in air or under protective gas, followed by cooling in a temperature range below 900°C under a vacuum of 1 to 50 HPa or under protective gas. When the cooling process is completed the dental prosthesis can be removed from the graphite box.

Heating to the sintering temperature and the sintering process in the graphite box are preferably carried out in air and the cooking process in the temperature range below 900°C is preferably carried out under vacuum. This is advantageous particularly because of the equipment normally present in a dental laboratory and also with regard to the costs.

Preferred times for the thermal treatment at temperatures of between 100 and 400°C and for the sintering process are 5 to 25 minutes and 10 to 30 minutes respectively.

When the work is not performed in a graphite box, then it must be carried out under protective gas. In the latter case the partiale oxygen pressure should be less than 5×10^{-2} HPa. This is assured, for example, when using industrially pure argon, and++ can be achieved by relatively simple reconstruction of a conventional ceramics kiln.

A special advantage of this process lies in that an adequately high density associated with closed porosity is attained with the above-mentioned parameters, particularly with the vacuum cooling even upon sintering repeatly.

In the process according to the present invention a mixture of predominantly spherical powders having a bimodal or multimodal particle size distribution is used. This powder mixture is mixed with a mixing fluid which substantially consists of water but may also contain small additions of electrolytes, as for example, strontium chloride, copper chloride or ammonium nitrate, monohydric or polyhydric alcohols, celluslose or polyethylene glycol, either by hand or with a stirrer suitable for this purpose so as to obtain a slip whose consistency and moulding properties correspond to those of conventional dental and facing ceramics.

The slip thus prepared is coated on a high temperature-resistant model of the teeth to be treated, applying the technology commonly used in dental ceramics. On said model the slip is compressed by means of conventional methods (for example, shaking with the grooved portion of a moulding instrument, ultrasound, etc). The fluid thus gets to the surface, which is cleaned off with a cloth or dried in a warm air stream. It is advisable to

impregnate or insulate the stump with a liquid prior to the application of the slip so that the moisture is not removed from the slip by the stump.

The green compact compressed to a high gross density is allowed to stand on the model in air for approximately 5 to 25 minutes in order to dry slowly. This can also clone on the top plate of a ceramics baking kiln that normally has temperature of $\leq 50^{o}C$. The dental prosthesis on the model is then put into a graphite box which completely encompasses the model.

The dental prosthesis is then subjected to a thermal treatment in an oven for 5 to 45 minutes at a temperature of between 100 and $400^{o}C$. The aim of this thermal treatment is the removal of moisture possibly still present or of organic impurities. If this thermal treatment is not carried out prior to the actual sintering process, this will result in the formation of cracks in the walls of the crown. When the temperature of $400^{o}C$ are exceeded and the temperature is maintained corresponding to the defined times, then the density of the sintered dental prosthesis will drop drastically.

On completion of the thermal treatment the graphite box with the dental prosthesis therein is heated to the sintering temperature. In order to attain a sufficiently high sintering density, it is necessary to bridge the temperature range of between $400^{o}C$ and $800^{o}C$ with an average heating rate exceeding 50 K per minute, particularly a rate of 50 to 300 K per minute.

Lower heating rates result in a reduced density. At temperatures above $800^{o}C$ it is favourable to select an average heating rate of between 20 and 200 K per minute. This results in acceptable times also with regard to the total sintering time.

The density of the sintered dental prosthesis depends on the sintering temperature T. Surprisingly it has been found that the

density has a maximum in the temperature range of between ($T_{solidus}$-200^oC) and ($T_{solidus}$-70^oC), the exact position depending in turn on the specific alloy. The maximum extends over a temperature range of 20 to 50^oC and a very substantial drop of the density values is observed on exceeding this maximum. Two typical curves for two powder mixtures are shown in the drawing.

The dental prosthesis in the graphite box can be sintered in air or under protective gas. The sintering process is preferably carried out in air since the results obtained are not poor than those obtained under protective gas and since the expenditure for equipment is comparatively lower.

The sintering time isi 5 to 45 minutes and as a rule the maximal density is attained at sintering times of as low as between 10 and 30 minutes.

Cooling the sintered dental prosthesis in the graphite box in air does not result in high densities after the first sintering step. However, for the production of bridges or for the correction of the occlusion, the contact points or of the edge end a second sintering step is required. Despite the identical sintering cycle the density of the sintered dental prosthesis decreases drastically upon sintering twice. Surprisingly it has now been found that by cooling the dental prosthesis in the graphite box under a vacuum of between 50 and 1 HPa the density drop upon sintering repeatedly can be prevented. However, it is crucial that the required vacuum is present before the dental prosthesis is cooled to a temperature < 900^oC.

The sintering process can also be carried out without a graphite box but in that case it must be carried out under protective gas and the above-mentioned data on temperature and time also apply. The partial oxygen pressure in the protective gas must not exceed 5 x 10^{-2} HPa in order to attain a sufficiently high density. The

cooling process must then also be carried out under protective gas.

The following Examples will illustrate the process according to the present invention:

Example 1

By adding a mixing fluid of 98% of H_2O and 2% of polyethylene glycol to the slip from the powder mixture 1 (Table 2) a consistency suitable for moulding was imparted to the slip. With the aid of a brush the slip is coated on a stump impregnated with a liquid. The crown is completely moulded and the slufe is checked again and again in the articulator.

The slip is compressed by grooving with a moulding instrument. The fluid emerging from the surface is removed with a cloth. The good stability of the slip allows the construction of details of the occlusal surface such as humps or troughs. After the compression (water no longer emerges from the surface) the surface can be reworked by scraping or carving so that fine fissures can also created prior to the sintering process. The completely moulded crown remains on the stump during the entire sintering process and is then placed on the cover plate of a ceramics oven in order to dry it. After 15 minutes it is put into a graphite box comprising a graphite bottom with a corresponding receptacle for the stump and a cup-shaped graphite cap. The graphite box with the moulded crown is put into an oven which is simultaneously heated to 300°C. After 15 minutes the graphite box is put into a ceramics baking kiln preheated to 1000°C. The temperature is increased to 1050°C. The sintering temperature of 1050°C is reached after 5 minutes corresponding to an average heating rate of 150 K per minute. The sintering temperature of 1050°C is 160°C below the $T_{solidus}$ temperature of 1210°C (see Table 2). After 20 minutes the graphite box is removed from the kiln and cooled in air. A number of small corrections are required on the occlusal surface and in an edge

region. The points to be corrected are subsequently marked on the sintered crown in the above described manner. The crown is then sintered once more, using the above-described sintering cycle. On checking the density a value of 14.2 g/cc is obtained. The crown is too large because it was cooled in air.

Example 2

A further crown is produced analogously to Example 1. However, on completion of the sintering process at 1050^{o}C the crown is transferred into a cooling chamber that can be evacuated. Immediately upon transferring the graphite box the cooling chamber is evacuated to a vacuum of approximately 50 HPa. After approximately 15 minutes the cooled specimen can be removed. As described in Example 1 a number of small corrections are made. The crown is sintered once more and again cooled under vacuum. The stump mass is blasted, using a sand blast apparatus and the density is determined. It now is 16.1 g/cc; the porosity is closed. The crown is perfected and polished. The edge fissure on the master model is on the average 40 m.

Example 3

For the production of inlays the powder mixture 2 (Table 2) is used since this alloy is yellow and is preferred by many patients. Furthermore, this alloy has a lower 0.2% offset yield strength and an increased ductility. This allows the edges to be more easily worked with pieces in the mouth. The production is carried out analogously to that of the process described in Example 2.

However, the sintering cycle is slightly modified. After being dried in air the inlay on the model stump (in the graphite box) is placed on the baking table of an open ceramics baking oven that has been preheated to 700^{o}C,. The temperature on the baking table is approximately 250^{o}C. After 9 minutes the baking table runs in automatically into the oven which heats up to the sintering temperature of 940^{o}C. After further 15 minutes the

specimen can be removed from the oven and transferred to the cooling chamber, where it is cooled under a vacuum of 50 HPa. The stump mass is blasted, the inlay is perfected, put on the master model stump and polished. The density is 17.1 g per ce and the porosity is closed. The pores located on the surface are closed by the polish. The edge fissure is approximately 50 m. The rate of change of temperature between 400 and $800^{o}C$ is on the average approximately 120 K per minute. The rate of change of temperature between $800^{o}C$ and the sintering temperature is on the average 100 K per minute. $T_{solidus}$ is $1040^{o}C$ (Table 2)

Palladium alloys can also be processed in the same manner.

The composition of the alloys used in the examples, their production, particle shape and particle size have been compiled in Table 1. The compositions of the powder mixtures used in the examples have been compiled in Table 2

The sintering density of the dental prosthesis parts according to the powder mixtures of Table 2 is shown in the drawing as a function of the sintering temperature.

TABLE 1
Examples of Powders Used

	Composition (mass proportion in %)	Particle Shape	Production	Particle Size/ m
Alloy 1	Au 65 Pt 15 Pd 13, In 2.5 + additives each <2%	predominantly spherical	atomization	-*
Alloy 2	Au 87 Pt 11 + additives each <2%	predominantly spherical	atomization	-*
Au Powder 1	Au	predominantly spherical	chemical precipitation	<5r
Au Powder 2	Au	predominantly spherical	chemical precipitation	<10

* depending on screening, always < 100 m

TABLE 2

	Component 1 powder content KG**/ m %	Component 2 powder content KG/ m %	Component 3 powder content KG/ m %	$T_{solidus}$*
Powder Mixture 1	alloy 1 80 < 63	Au 1 20 < 5		1210°C
Powder Mixture 2	alloy 2 85 < 50	Au 1 13 < 5	Au 2 2 < 10	1040°C

* $T_{solidus}$ of the sintered alloy

** KG = particle size

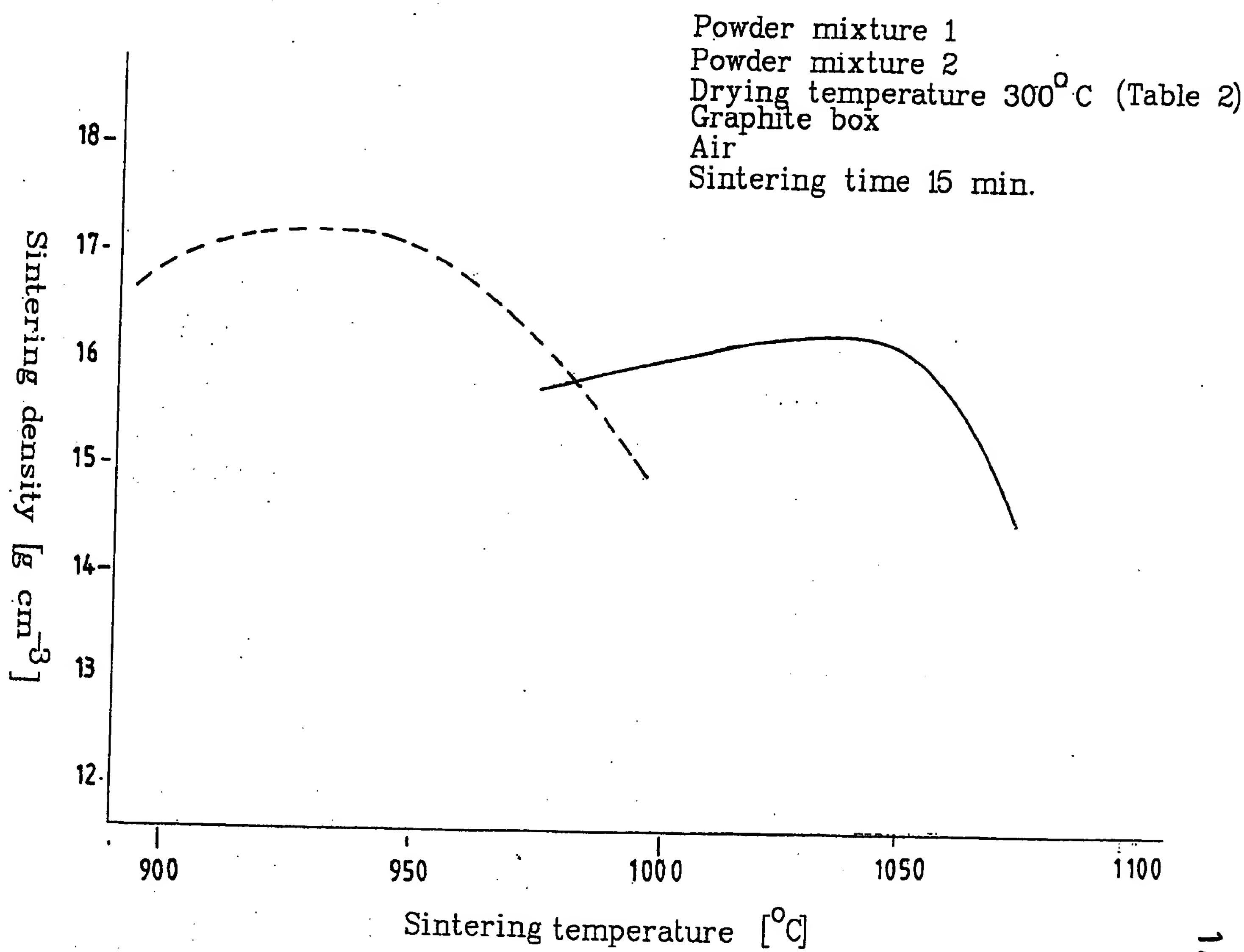
THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A process for producing a sintered dental prosthesis having a metallic structural matrix of a noble metal or of a noble metal alloy powder mixture with bimodal or multimodal particle size distribution and a predominantly spherical shape, said mixture being stirred with a mixing fluid consisting substantially of water to a slip capable of being moulded and compressible by expelling the mixing fluid, the prosthesis being moulded with said slip on a model of the teeth to be treated, applying the technology used in dental ceramics, said model serving as burner support, said slip subsequently being sintered on the model in a graphite box or under a protective gas, in which the moulded dental prosthesis is first dried in air for 5 to 25 minutes and then subjected to thermal treatment for 5 to 45 minutes at temperatures of between 100 and 400°C, whereupon it is heated to 800°C at an average temperature increase of 50 to 300 K per minute and above 800°C it is heated to the sintering temperature T at an average temperature increase of 20 to 200 K per minute in air in the graphite box or under a protective gas, said sintering temperature T lying between ($T_{solidus}$- 200°C) and ($T_{solidus}$-70°C). $T_{solidus}$ being the solidus temperature of the sintered alloy, the sintering process is carried out at this temperature for 5 to 45 minutes in the graphite box in air or under a protective gas and thereafter cooling is applied at temperatures of between 800°C and room temperature under a protective gas or when using a graphite box even under a vacuum of 50 to 1 HPa.

2. A process according as claimed in claim 1, wherein the thermal treatment is carried out at temperatures of between 100 and 400°C for 5 to 25 minutes and the sintering step is carried out for 10 to 30 minutes.

3. A process as claimed in claim 1 or 2, wherein the step of heating to the sintering temperature, the sintering and the cooling are carried out under a protective gas under a partial oxygen pressure lower than 5×10^{-2} HPa.

4. A process as claimed in claim 1 or 2 in which the heating to the sintering temperature and the sintering of the graphite box are carried out in air and the cooling in the temperature range below $900^{\circ}C$ is carried out under vacuum.


Powder mixture 1
Powder mixture 2
Drying temperature 300°C (Table 2)
Graphite box
Air
Sintering time 15 min.
Sintering density [g cm-3]
18
17
16
15
14
13
12
900
950
1000
1050
1100
Sintering temperature [°C]